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(54) **Degradable laminate composition**

Abbaubare Schichtstoffzusammensetzung

Composition dégradable de produits stratifiés

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## Description

The present invention relates to a laminated composition comprising a thermoplastic polymer having degradability in the natural environment and a regenerated cellulose film (cellophane), paper, leather, cloth or fiber. More particularly, the invention relates to a degradable, laminated composition comprising a polymer comprising polylactic acid or a lactic acid-hydroxycarboxylic acid copolymer and cellophane, paper, leather, cloth or fiber. The laminated composition can be used for moisture-proof packaging papers, decorative papers, containers for milk and juice, and other packaging materials. These materials can be readily degraded after use in the natural environment.

The use of packaging plastics has recently increased because of considerations of attractive appearance, hygiene, packaging and transport of commodities. As a result of this trend, the amount of refuse discarded from households and factories has rapidly increased and shortages of waste burial sites have caused a serious problem around cities.

Materials such as regenerated cellulose film (called cellophane), paper, leather, natural fiber or cloth prepared from natural fiber are degradable in the natural environment. They are degraded in a long period though buried under the ground, and do not develop hazardous gas in the case of incineration. Some of them are recovered and reused in view of resource protection. Thus these degradable materials are used for disposable wrapping papers, containers and other various packaging materials in place of difficultly degradable plastics, and are expected to have increased uses in the future.

However, a laminated composition comprising a thermo-plastic polymer having degradability in the natural environment and a regenerated cellulose film (cellophane), paper, leather, cloth or fiber has not yet been known.

Cellophane is substantially in demand as a packaging material which is excellent in transparency, impermeability to gases, easy printability and gloss. However, cellophane is inferior in moisture-proofness, low-temperature resistance, strength and heat-sealing characteristic, and hence is usually used by laminating with a synthetic polymer in order to compensate for these drawbacks. Packaging papers and paper containers have low strength and poor water resistance and thus paper packs and paper cups for milk and juices are prepared from laminated paper obtained by laminating a polymer and paper. Book covers and dressing cases are generally prepared from laminated paper having smooth surface and gloss in order to satisfy a desire of the consumer for beauty. Leather, cloth and fiber are also used for wrapping papers, containers and other various packaging materials as principal or secondary components and have similar disadvantages.

Polymers used for these purposes have been poly-

olefins such as polyethylene and polypropylene, and paper-coating polyester. These polymers, however, have almost no degradability in the natural environment. When their laminates are abandoned and buried under the ground, these polymers greatly lower degradation rates of cellophane, paper, leather and cloth which are substantially degradable in the natural environment. A large amount of heat generation in the incineration of these polymers leads to problems such as damage to furnaces. When the laminates are recovered, problems occur in separating these polymers.

Polylactic acid and lactic acid copolymers have recently become known as thermoplastic and biodegradable polymers. These lactic acid polymers can be completely biodegraded within several months to a year in an animal body. When the polymers are placed in soil or sea water, the polymers start to decompose within several weeks in a moist environment and disappear in about a year. The degradation products of these polymers are lactic acid, carbon dioxide and water, and all of these compounds are nontoxic.

US patents 1,995,970, 2,362,511, and 2,683,136 have disclosed a polymerization process of lactic acid. US patents 3,636,956 and 3,797,499 have disclosed a process for copolymerizing lactic acid and glycolic acid. Polymers of lactic acid are usually prepared from a cyclic dimer of lactic acid which is called lactide. In the copolymerization of lactic acid, lactide and glycolide (a dimer of glycolic acid) are mixed and ring-opening polymerization is carried out. When the polymer is directly prepared through dehydrating condensation from lactic acid or a mixture of lactic acid and glycolic acid, a high molecular weight polymer cannot be obtained even though the reaction is carried out for a long time. On the other hand, the ring-opening polymerization of lactide or of a mixture of lactide and glycolide can provide a high molecular weight straight-chain polyester.

GB-A-1,397,570 concerns a water-soluble container made of a laminate having a relatively thick core of a water-soluble thermoplastics material, protected on one or both sides by a removable protective layer. Thus for disposal, the protective layer is peeled off and the core can be dissolved in cold water. Generally the core is of hydroxypropyl cellulose, through polylactic acid is also mentioned. Generally the protective layers are conventional thermoplastics such as polyethylene, through other materials including cellophane and waxed paper are also mentioned.

According to the present invention there is provided a degradable laminate comprising a surface layer of a thermoplastic, degradable polymer having an average molecular weight of from 10,000 to 1,000,000 comprising polylactic acid, a copolymer of lactic acid and a different hydroxycarboxylic acid or a mixture of polylactic acid with a polymer of a different hydroxycarboxylic acid or with a copolymer of lactic acid and a different hydroxycarboxylic acid, laminated to the surface of a regener-

ated cellulose film, paper, leather, or cloth.

Embodiments of the invention desirably provide a laminate including a layer of a polymer which can be degraded with ease in the natural environment and generates harmless degradation products. The inventors have found out that a polymer comprising, or essentially consisting of, polylactic acid or a copolymer of lactic acid and a different hydroxycarboxylic acid can be strongly adhered to a substrate such as cellophane, paper, leather or cloth by adhering or applying the polymer to the substrate in the form of a film or a solution, and further that the laminated composition is excellent in transparency, gloss and moisture-proofness, and has high mechanical strength.

The raw materials of the polymer are lactic acid, lactide which is a cyclic dimer of lactic acid, and other hydroxycarboxylic acids. Other hydroxycarboxylic acids include, for example, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid and 6-hydroxycaproic acid. Other materials can be used as a mixture, if desired.

These polymers can be directly prepared through dehydrating polycondensation from lactic acid or other hydroxycarboxylic acid or through ring-opening polymerisation from lactide, glycolide,  $\epsilon$ -caprolactone or a mixture of these compounds. A copolymer prepared by transesterification of polylactic acid with other hydroxycarboxylic acid polymers can also be used. The lactic acid unit which constituted these polymers can be L-lactic acid, D-lactic acid or a mixture of these lactic acids.

The polymer has an average molecular weight of from 10,000 to 1,000,000. The polymerization degree is generally from 150 to 20,000. The average molecular weight lower than this range leads to low strength of processed products such as film and hence is unsuitable for practical use. When the average molecular weight is higher than this range, processing ability becomes poor because of high viscosity in the hot-melted state.

Plasticizers can be added in order to provide flexibility for the above polymers. Plasticizers which can be used include, for example, diethyl phthalate, dioctyl phthalate, dicyclohexyl phthalate and other phthalic acid esters; di-isobutyl adipate, di-n-octyl adipate, di-n-butyl sebacate, di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate and other aliphatic dicarboxylic acid esters; diphenyl 2-ethylhexyl phosphate, diphenyl octyl phosphate and other phosphoric acid esters; tributyl acetylacrylate, tri-2-ethylhexyl acetylacrylate, tributyl citrate and other hydroxypolycarboxylic acid esters; methyl acetylricinoleate, amyl stearate and other aliphatic carboxylic acid esters; glycerol triacetate, triethylene glycol dicaprylate and other polyhydric alcohol esters; epoxylated soybean oil, octyl epoxystearate and other epoxy-base plasticizers; and polypropylene glycol adipate, polypropylene glycol sebacate and other polyester base plasticizers. Safe plasticizers are preferably used for food packaging containers.

The amount of the plasticizer for use is usually from 5 to 50% by weight, preferably from 5 to 20% by weight for the polymer composition. The plasticizer is added to the polymer as a solution in a solvent or in molten state.

No particular restriction is imposed on the regenerated cellulose used for the laminated composition of the invention. Common cellophane and moisture-proof cellophane may be used.

Exemplary paper for use in the invention includes art paper (coated paper), kraft paper, rolled sheet, rice paper, and other processing base-paper, cross paper and paper-board. The above paper may contain regenerated pulp.

The leather used in the invention is a natural product, and parchment-like thin leather and thick leather can both be used.

The cloth for use in the invention is desirably a cloth prepared from natural fiber.

Exemplary natural fibers includes cotton, silk and wool. The cloth includes bands and may be textiles or nonwoven fabrics. The cloth is preferably composed of natural products but may contain artificial materials, if desired.

Lamination can be carried out by various method such as solution coating, hot-melt coating, and extrusion lamination.

When an adhesive is used, it is preferred to use a decomposable adhesive such as glue, gelatin, casein and starch. However, some kinds of paper do not use adhesive in order to avoid disturbance for the degradation of the laminated composition. The surface of cellophane, paper, leather or cloth can also be anchored prior to lamination with an organic titanium compound, organic silane compound or polyethyleneimine. In some cases, paper can be previously impregnated with lactic acid, other hydroxycarboxylic acid, lactide, glycolide or  $\epsilon$ -caprolactone.

The degradable, laminated composition of the present invention can be further laminated with other films, for example, aluminum foil.

The present invention will hereinafter be illustrated in detail by way of examples. However, these examples are not intended to limit the scope of the present invention.

#### EXAMPLE 1

A cellophane film having dimensions of 150 x 150 mm and a thickness of 50  $\mu$ m was coated with a 30 % aqueous gelatin solution as an adhesive. A polymer film having a thickness of 30  $\mu$ m was prepared from poly-L-lactic acid having a weight average molecular weight of 150,000, overlapped on the gelatin-coated surface, pressed overnight under pressure of 1 kg/cm<sup>2</sup> and then dried at 60 °C for a day.

Adhesion between cellophane and the polymer film was good, and a laminated film thus obtained was strong.

The laminated film was buried in a compost at 40 °C for 2 months. After the test, the polymer film on the surface was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 2

A cellophane film having dimensions of 150 × 150 mm and a thickness of 50 µm was overlapped with the same poly-L-lactic acid film as used in Example 1 and pressed at 200°C for 5 minutes under the pressure of 30 kg/cm<sup>2</sup>.

The laminated film thus obtained had good adhesion between the cellophane and the polymer films, and was strong and good in surface gloss.

The laminated film was buried in a compost at 40°C for 2 months. After the test, the polymer film was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 3

A laminated film was prepared by carrying out the same procedures as described in Example 2 except that the poly-L-lactic acid film was replaced by a film which had a thickness of 25 µm and was prepared from a copolymer having a weight average molecular weight of 110,000 and consisting of L- and D-lactic acid in a ratio of 9 : 1.

Adhesion between cellophane and the polymer film was good, and a laminated film thus obtained was strong and had good surface gloss.

The laminated film was buried in a compost at 40°C for 2 months. After the test, the polymer film on the surface was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 4

A laminated film was prepared by carrying out the same procedures as described in Example 2 except that the poly-L-lactic acid film was replaced by a film which had a thickness of 25 µm and was prepared from a copolymer having a weight average molecular weight of 50,000 and consisting of L-lactic acid and glycolic acid in a ratio of 1 : 1.

Adhesion between cellophane and the polymer film was good, and the laminated film thus obtained was strong and had good surface gloss.

The laminated film was buried in a compost at 40°C for 2 months. After the test, the polymer film on the surface was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 5

A laminated film was prepared by carrying out the same procedures as described in Example 2 except

that the poly-L-lactic acid film was replaced by a film which had a thickness of 25 µm and was prepared from a copolymer having a weight average molecular weight of 60,000 and consisting of L-lactic acid and 6-hydroxycaproic acid in a ratio of 1 : 1.

Adhesion between cellophane and the polymer film was good and the laminated film obtained was strong and had good surface gloss.

The laminated film was buried in a compost at 40°C for 2 months. After the test, the polymer film was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 6

A cellophane film having dimensions of 150 × 150 mm and a thickness of 50 µm was coated with 2.0 g of a 15 % chloroform solution of poly-L-lactic acid having a molecular weight of 110,000 and dried overnight at the room temperature.

The laminated film was buried in a compost at 40 °C for a month. After the test, the polymer film was deteriorated and could be crushed with ease by external force.

#### EXAMPLE 7

A kraft paper having dimensions of 150 × 150 mm and a basis weight of 82 g/m<sup>2</sup> was coated with a 30 % aqueous gelatin solution as an adhesive, overlapped with a film which was prepared from poly-L-lactic acid having a weight average molecular weight of 150,000 and had thickness of 30 µm, and pressed overnight under the pressure of 1 kg/cm<sup>2</sup>.

Adhesion between the paper and the polymer film was good and the laminated paper obtained was strong. The laminated paper was heated to 60°C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution, and the residual paper portion could be torn with ease.

The laminated paper was buried in a soil for a month. After the test, the film on the surface was deteriorated and could be torn with ease.

#### EXAMPLE 8

A wood free paper having dimensions of 150 × 150 mm and a basis weight of 65.5 g/m<sup>2</sup> was overlapped with a poly-L-lactic acid film as used in Example 7 and pressed at 200°C for 3 minutes under the pressure of 30 kg/cm<sup>2</sup>.

Adhesion between the paper and the polymer film was good, and the laminated film obtained was strong and had good surface gloss.

The laminated film was heated to 60°C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the

solution, and the residual paper portion was buried in a soil for a month.

After the test, the film on the surface was deteriorated and could be torn with ease.

#### EXAMPLE 9

A laminated paper was prepared by carrying out the same procedures as described in Example 8 except that the poly-L-lactic acid film was replaced by a film which was prepared from a copolymer having a weight average molecular weight of 110,000 and consisting of L-lactic acid and D-lactic acid in a ratio of 1 : 1 and had a thickness of 25  $\mu\text{m}$ .

Adhesion between the paper and the polymer film was good. The laminated film obtained was strong and had good surface gloss.

The laminated paper was heated to 60 °C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution, and the residual paper portion could be torn with ease.

The laminated paper was buried in a soil for a month. After the test, the polymer film on the surface was deteriorated and could be torn with ease.

#### EXAMPLE 10

A laminated paper was prepared by carrying out the same procedures as described in Example 8 except that the poly-L-lactic acid film was replaced by a film which was prepared from a copolymer having a weight average molecular weight of 50,000 and consisting of L-lactic acid and glycolic acid in a ratio of 1 : 1 and had a thickness of 25  $\mu\text{m}$ .

Adhesion between the paper and the polymer film was good. The laminated film obtained was strong and had good surface gloss.

The laminated paper was heated to 60 °C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution, and the residual paper portion could be torn with ease.

The laminated paper was buried in a soil for a month. After the test, the polymer film on the surface was deteriorated and could be torn with ease.

#### EXAMPLE 11

A laminated paper was prepared by carrying out the same procedures as described in Example 8 except that the poly-L-lactic acid film was replaced by a film which was prepared from a copolymer having a weight average molecular weight of 60,000 and consisting of L-lactic acid and 6-hydroxycaproic acid in a ratio of 1 : 1 and had a thickness of 25  $\mu\text{m}$ .

Adhesion between the paper and the polymer film was good. The laminated film obtained was strong and

had good surface gloss.

The laminated film was heated to 60°C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution, and the residual paper portion could be torn with ease.

The laminated paper was buried in a soil for a month. After the test, the film on the surface was deteriorated, and could be torn with ease.

#### EXAMPLE 12

To a wood free paper having dimensions of 150 × 150 mm and a basis weight of 65.5g/m<sup>2</sup>, 2.0g of a 15% chloroform solution of poly -L-lactic acid having a molecular weight of 110,000 was applied and dried overnight at the room temperature. The laminated composition thus obtained was further dried at 50 °C under reduced pressure. The laminated paper thus obtained was strong and had good surface gloss.

The laminated paper was heated to 60 °C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution and the residual paper portion could be torn with ease.

The laminated paper was buried in a soil for a month. After the test, the film on the surface was deteriorated and could be torn with ease.

#### EXAMPLE 13

A parchment having dimensions of 150 × 150mm and a thickness of 500  $\mu\text{m}$  was coated with an aqueous casein solution as an adhesive. A film which was prepared from poly-L-lactic acid having a weight average molecular weight of 150,000 and had a thickness of 30  $\mu\text{m}$  was overlapped on the coated surface and pressed overnight at the room temperature under pressure of 5 kg/cm<sup>2</sup> and successively dried at 60 °C for a day.

Adhesion between the parchment and the polymer film was good and the laminate thus obtained was strong.

The laminate was heated to 60°C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer layer on the surface was dissolved into the solution, and the parchment was recovered and could be reused.

#### EXAMPLE 14

A cotton cloth having dimensions of 150×150 mm and a thickness of 300  $\mu\text{m}$  was treated with glyoxal, overlapped with a film which was prepared from poly-L-lactic acid having a weight average molecular weight of 150,000 and had a thickness of 30  $\mu\text{m}$ , pressed overnight at the room temperature under pressure of 5kg/cm<sup>2</sup>, and thereafter dried at 60°C for a day.

Adhesion between the cotton cloth and the polymer film was good and the laminate thus obtained was

strong.

The laminated was heated to 60°C in a 1 N aqueous sodium hydroxide solution. After an hour, the polymer film on the surface was dissolved into the solution, and the cotton cloth was recovered.

#### EXAMPLE 15

A polyamino acid fiber having a thickness of 50 µm was passed through a 15% chloroform solution of poly-L-lactic acid having a molecular weight of 110,000 to adhere poly-L-lactic acid to the surface of the fiber. After drying, the treated fibers were lengthwise and crosswise combined and hot pressed to obtain a nonwoven fabric.

A film which was prepared from poly-L-lactic acid having a weight average molecular weight of 150,000 and had a thickness of 30 µm was overlapped on the above-obtained nonwoven fabric having dimension of 150x150mm and a thickness of 200 µm, pressed overnight at the room temperature under the pressure of 5 kg/cm<sup>2</sup> and successively dried at 60°C for a day.

Adhesion between the nonwoven fabric and the polymer film was good. The laminated sheet thus obtained was strong.

The laminated sheet was buried in a compost at 40°C for 2 months. After the test, the sheet was deteriorated and the shape of the sheet was destroyed with ease by external force.

#### Claims

1. A degradable laminate comprising a surface layer of a thermoplastic, degradable polymer having an average molecular weight of from 10,000 to 1,000,000 comprising polylactic acid, a copolymer of lactic acid and a different hydroxycarboxylic acid or a mixture of polylactic acid with a polymer of a different hydroxycarboxylic acid or with a copolymer of lactic acid and a different hydroxycarboxylic acid, laminated to the surface of a regenerated cellulose film, paper, leather, or cloth.
2. A laminate according to claim 1 wherein the thermoplastic polymer consists essentially of polylactic acid, a copolymer of lactic acid and a different hydroxycarboxylic acid or a mixture of polylactic acid with a polymer of a different hydroxycarboxylic acid or with a copolymer of lactic acid and a different hydroxycarboxylic acid.
3. The laminate of claim 1 or 2 wherein said lactic acid is D-lactic acid, L-lactic acid or a mixture thereof.
4. The laminate of any one of claims 1 to 3 wherein said different hydroxycarboxylic acid is glycolic acid or 6-hydroxycaproic acid.

#### Patentansprüche

1. Abbaubares Laminat, umfassend eine Oberflächenschicht aus einem thermoplastischen, abbaubaren Polymer mit einem durchschnittlichen Molekulargewicht von 10.000 bis 1.000.000, das Polymilchsäure, ein Copolymer von Milchsäure mit einer anderen Hydroxycarbonsäure oder ein Gemisch aus Polymilchsäure und einem Polymer einer anderen Hydroxycarbonsäure oder einem Copolymer von Milchsäure mit einer anderen Hydroxycarbonsäure umfaßt, auflaminiert auf die Oberfläche eines Regeneratcellulosefilms, von Papier, Leder oder Stoff.
2. Laminat nach Anspruch 1, worin das thermoplastische Polymer im wesentlichen aus Polymilchsäure, einem Copolymer von Milchsäure mit einer anderen Hydroxycarbonsäure oder einem Gemisch aus Polymilchsäure und einem Polymer einer anderen Hydroxycarbonsäure oder einem Copolymer von Milchsäure mit einer anderen Hydroxycarbonsäure besteht.
3. Laminat nach Anspruch 1 oder 2, worin die Milchsäure D-Milchsäure, L-Milchsäure oder ein Gemisch davon ist.
4. Laminat nach einem der Ansprüche 1 bis 3, worin die andere Hydroxycarbonsäure Glykolsäure oder 6-Hydroxycapronsäure ist.

#### Revendications

1. Laminé dégradable comprenant une couche de surface d'un polymère dégradable, thermoplastique ayant un poids moléculaire moyen de 10 000 à 1 000 000 comprenant de l'acide polylactique, un copolymère d'acide lactique et un acide hydroxycarboxylique différent ou un mélange d'un acide polylactique avec un polymère d'un acide hydroxycarboxylique différent ou avec un copolymère d'acide lactique et un acide hydroxycarboxylique différent, laminé à la surface d'un film de cellulose régénérée, de papier, de cuir ou d'une pièce de tissu.
2. Laminé selon la revendication 1 dans lequel le polymère thermoplastique consiste essentiellement en un acide polylactique, un copolymère d'acide lactique et un acide hydroxycarboxylique différent ou un mélange d'un acide polylactique avec un polymère d'un acide hydroxycarboxylique différent ou avec un copolymère d'acide lactique et un acide hydroxycarboxylique différent.
3. Le laminé selon la revendication 1 ou 2 dans lequel ledit acide lactique est l'acide D-lactique, l'acide L-

lactique ou un mélange de ceux-ci.

4. Laminé selon l'une quelconque des revendications 1 à 3 dans lequel ledit acide hydroxycarboxylique différent est l'acide glycolique ou l'acide 6-hydroxycaproïque.

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